higher, and the reorientational frequency at the melting point is a factor of 3.5 smaller than for benzene. Lack of charge transfer between bromine and benzene in the complex is demonstrated by the magnitude of the bromine NQR frequency. The strong temperature dependence of ν_Q indicates anomalously large thermal motion of bromine in the complex. A phase transition occurs near 60°K as evidenced by a discontinuity in ν_Q. It seems likely that the complex is bound by van der Waals and electrostatic multipole interactions. This is indicated since the distance of the nearest bromine atom from the plane of the benzene ring is observed[2] to be 3.36 Å. From the van der Waals radii[8] of aromatic carbon and bromine, one calculates 3.36 Å for this distance.

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Studies of the 3455-Å Triplet State of *s*-Triazine*

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We present a confirmation of the assignment of the 28 935-cm^{-1} triplet state, $^3A_1''$, of *s*-triazine. The high-field Zeeman effect is used to make this assignment which is consistent with the fact the transition is polarized perpendicular to the molecular plane. The optical spectrum at low magnetic fields yields the zero-field splitting $D=-0.058\pm0.024$ cm^{-1}. The sign and magnitude of D is consistent with an $n\pi^*$ state in which one-center spin–spin interaction is a significant feature of the zero-field splitting.

INTRODUCTION

s-Triazine is an important prototype not only because of its high symmetry and resemblance to benzene, but also because the low-lying electronic states are expected to be numerous and to display properties of both π and nonbonding electrons in addition to interactions between them. Existing experiments on the low-energy states of *s*-triazine are mainly from low resolution solution spectra,[1,2] and the characterization of these states and their relations to theory[3,4] are not yet established.

A phosphorescence at about 4500 Å was attributed to *s*-triazine,[1] but in some earlier work[5] we have been unable to find a triplet state of the *s*-triazine crystal at lower energy than 3455 Å. Hochstrasser and Lin[5] have presented a succinct summary of some properties of the 3455-Å triplet state: It was assigned from Zeeman effects to be $^3A_1''$, hence $n\pi^*$, and the zero-field splitting was estimated to be about $D=-0.05$ cm^{-1}.

The triazine crystal is nearly uniaxial at low temperatures,[6,7] and so optical spectroscopy in polarized light and magnetic fields lends itself to particularly straightforward interpretation. In the present study we provide precise measurements of the polarization, the high-field and the low-field Zeeman effects of the 3455-Å triplet state of the *s*-triazine crystal, leading to a strengthening of the assignment for this state, and to proper limits for its zero-field splitting. The latter measurement is particularly important because of the apparent difficulty in obtaining phosphorescence from the $^3A_1''$ state, and hence in making a conventional EPR study.

We also present a brief account of the development of the $n\pi^*$ states of *s*-triazine; leading to a one-center computation of the spin–spin interaction in a $^3A_1''$ state.

EXPERIMENTAL

The *s*-triazine was obtained from the Aldrich Chemical Company then purified by zone refining. The purified *s*-triazine was sublimed into crystal growing tubes and large single crystals grown by the Bridgeman method. Crystals with good cleavage and low light scattering were only obtained when a very slow growth rate (1 mm/h) was employed. Oriented crystals were placed in a rotatable mount in the field of a superconducting magnet. The spectra were photoelectrically recorded on a 2-m Jarrell–Ash Czerny–Turner–Fastie spectrograph at a dispersion of 5.4 Å/cm at 3455 Å in the 16th order. The spectral accuracy in these measurements was about 0.05 cm^{-1}.

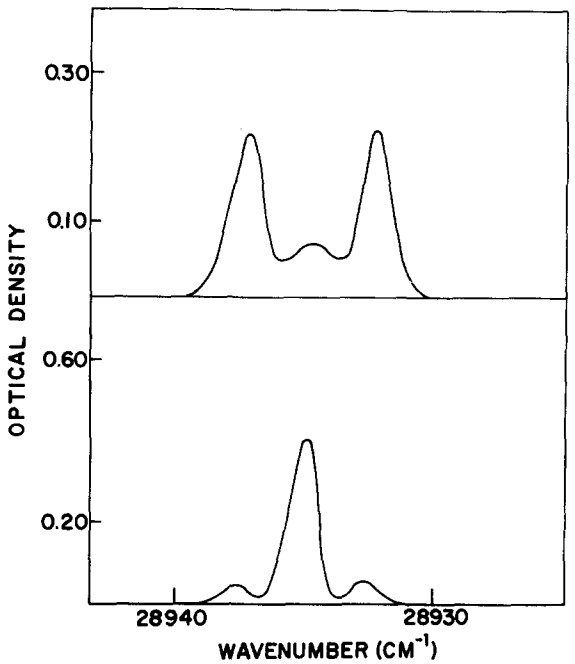

FIG. 1. Absorption spectra of the *s*-triazine single crystal at 4.2°K. The 0, 0 band spectra are for $H=27.5$ kG. Upper: the magnetic field is perpendicular to the optic axis. Lower: the magnetic field is parallel to the optic axis.

The crystals were oriented conoscopically. The crystals are uniaxial[6,7] above 213°K and so only the optic axis needs to be identified. Apparently there is a transition to a monoclinic phase below 213°K, but the large single crystals retain their optical quality even on cooling to 4.2°K. Below 213°K there is a triple twinning[7] and the three substructures have their monoclinic *c* axes regularly disposed (threefold symmetry) about the direction of *c* axis of the uniaxial form. The angle between the monoclinic and uniaxial *c* axes is 6° so that the optical absorption properties are expected to be only slightly influenced by this phase change.

TRIAZINE $\pi\pi^*$ AND $n\pi^*$ STATES

Excluding the contributions of bonding molecular orbitals to the nitrogen "lone-pair" wavefunctions in *s*-triazine, there arise three *n*-type molecular orbitals, each of which is a symmetry-determined function of the localized nonbonding orbitals σ_1, σ_3, and σ_5 corresponding to nitrogens at ring positions 1, 3, and 5. In the notation of Innes, Byrne, and Ross[8] these MO's are labeled according to whether atoms (*a*) or bonds (*b*) intersect the node,

$$\begin{aligned} n_0&=3^{-1/2}(\sigma_1+\sigma_3+\sigma_5),\\ n_a&=2^{-1/2}(\sigma_5-\sigma_3),\\ n_b&=6^{-1/2}(2\sigma_1-\sigma_3-\sigma_5); \end{aligned} \tag{1}$$

n_a and n_b are partners in the e' representation of D_{3h}. The real π and π^* orbitals have nodal properties like those of benzene; namely, π_0, (π_a, π_b), (π_{ab}, π_{bb}), π_{bbb}, where the bracketed pairs consist of partners in the e'' representation. The properly symmetrized linear combinations arising from the promotions $(n_a, n_b)\rightarrow(\pi_{ab}, \pi_{bb})$ are found, using projection operators, to be

$$\begin{aligned} \psi(A_1'')&=2^{-1/2}(n_b\pi_{ab}-n_a\pi_{bb}),\\ \psi(A_2'')&=2^{-1/2}(n_b\pi_{ab}+n_a\pi_{bb}),\\ \psi(E'')&=2^{-1/2}(n_b\pi_{bb}\pm n_a\pi_{ab}). \end{aligned} \tag{2}$$

The *n* and π orbitals are readily transformed into the alternative complex form with phase factors $\epsilon(e^{2\pi i/3})$ and ϵ^* amongst the basis orbitals. The functions n_a and n_b transform into the partners (n_2, n_{-2}), where

$$\begin{aligned} n_2&=3^{-1/2}(\sigma_1+\epsilon^*\sigma_3+\epsilon\sigma_5),\\ n_{-2}&=n_2^*. \end{aligned} \tag{3}$$

The subscripts refer to the index k in $C_3n_k=\epsilon^{k/2}n_k$. The π orbitals can be similarly projected using the complex form for the elements of the matrices of the irreducible representations of D_{3h}. The resulting functions have the form of the benzene orbitals π_0, (π_1, π_{-1}), (π_2, π_{-2}), π_3, where $\pi_k=\pi_{-k}^*$ and the degenerate pairs have e'' symmetry. The promotions $(n_{+2}, n_{-2})\rightarrow(\pi_{+2}, \pi_{-2})$ give the following combinations of configurations:

$$\begin{aligned} \psi_0(A_1'')&=2^{-1/2}(n_{-2}\pi_2-n_2\pi_{-2}),\\ \psi_0(A_2'')&=2^{-1/2}(n_{-2}\pi_2+n_2\pi_{-2}),\\ \psi_{\pm4}(E'')&=n_{\pm2}\pi_{\pm2}. \end{aligned} \tag{4}$$

There will be also excited configurations corresponding to $n_0\rightarrow\pi_{\pm2}$ promotions: Transitions to these E'' states will be forbidden but we do not necessarily expect them in the same spectral region as the A_1'', A_2'' and E'' states forming the $e'\otimes e''$ set. The transformations between the real and complex forms is made by the substitutions $n_a=i2^{-1/2}(n_{+2}-n_{-2})$ and $n_b=2^{-1/2}(n_{+2}+n_{-2})$. The foregoing results differ from those of Brinen and Goodman.[4]

ASSIGNMENT OF THE LOWEST OBSERVED TRIPLET STATE IN SINGLE CRYSTALS OF TRIAZINE

We herewith confirm the assignment of the 28 935-cm^{-1} transition of *s*-triazine as a $^3A_1''\leftarrow{}^1A_1'(\pi^*\leftarrow n)$ transition. This assignment is based on an analysis of the high-field Zeeman effects of the singlet–triplet absorption of neat triazine crystals and on the polarization of the absorption spectrum. The results are shown in Fig. 1: The presence of transitions to mainly $m_s=\pm1$ states with the field perpendicular to the optic axis of the crystal, and the virtual absence of these transitions when the field is parallel to the optic axis indicates that *the nondegenerate spin sublevel is predominantly radiatively active.* At zero field the substates have e'' and

a_2' spin symmetry in D_{3h} and we find that at least 85% of the transition intensity is polarized out of the molecular plane and corresponds to transitions involving a_2'. Because the singlet–triplet absorption spectrum is polarized out of plane (i.e., parallel to the optic axis of the crystal) the total symmetry of the upper state is A_2'' and hence the orbital designation is $A_1''(a_2'\otimes A_2'')$.

OPTICAL MEASUREMENT OF ZERO-FIELD SPLITTING

Because of the nearly uniaxial symmetry of the s-triazine crystal the optical spectroscopic measurement of the zero-field splitting can be made with reasonable precision. The previous estimate[5] was made from photographic tracings and it was not presented with standard error limits. In the present work we have made careful measurements of the intensity of absorption at 28 935 cm^{-1} in weak magnetic fields. We assume that the spin Hamiltonian for in-plane magnetic fields is

$$\mathcal{H}_s=\tfrac{1}{2}\gamma S_x+D(S_z^2-\tfrac{1}{3}S^2), \tag{5}$$

where $\gamma=2g\beta H$ with $g=2$. Then for z-polarized absorption the intensity ratio for transitions to the nearly $m_s=1$ vs the nearly $m_s=-1$ states is given by

$$I(+)/I(-)=[(2-D\gamma^{-1})/(2+D\gamma^{-1})]^2. \tag{6}$$

The experimental results are shown in Fig. 2. The most accurate numbers refer to a magnetic field of 16.5 kG directed perpendicular to the optic axis of the crystal, and the intensity ratio measured was $I(+)/I(-)=1.038\pm0.015$. Clearly the z-spin state (a_2') lies at higher energy than the degenerate pair, and we compute $D=-0.058\pm0.024$ cm^{-1}. As noted previously this zero-field splitting is small for an aromatic, and we accept this as further confirmation that the state is not a $\pi\pi^*$ benzenelike state (analogous to $^3B_{1u}$ of benzenes where $D\approx+0.15$ cm^{-1}). It should be pointed out that although the assignment of the triplet state as $^3A_1''$ is dependent on the polarization results not being severely influenced by certain kinds of crystal-field perturbations on the molecular levels, the zero-field splitting results do not depend on that assignment.

CALCULATION OF THE ZERO-FIELD SPLITTING

The purpose of this calculation is to evaluate the proposition that spin–spin magnetic dipole interaction can account for the approximate magnitude *and* sign of D. Since this is a less than common four-electron problem we will highlight the molecular-orbital approach to the calculation of D. The excited configuration is assumed to be $\psi_0(A_1'')$, and for the calculation the state $\Psi(A_1'')$ is written as a linear combination of Slater determinants for four electrons [i.e., the orbitals n_2, n_{-2}, π_2, and π_{-2} are included, with the open shells determined by Eqs. (4)] including the spin, such that

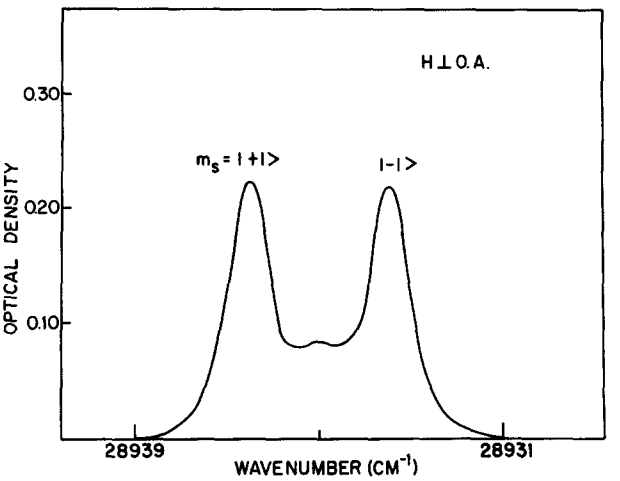

FIG. 2. Absorption spectrum of the $^3A_1''\leftarrow{}^1A_1'$ 0, 0 band in an s-triazine single crystal at 4.2°K. The light is propagating perpendicular to the optic axis and the magnetic field strength is 16.5 kG, directed perpendicular to the optic axis.

$\Psi_j(A_1'')$ is the state with $m_s=j$ ($j=0,\ \pm1$). The spin–spin dipole interaction operator $\mathcal{H}_D$ includes interactions between all electron pairs μ, ν,

$$\mathcal{H}_D=\hbar^{-2}\sum_{\mu<\nu}\sum_{q,q'}\Lambda_{qq'}(\mu,\nu)S_{\mu q}S_{\nu q'}. \tag{7}$$

The Cartesian coordinates of the electrons are labeled q, q', and $\Lambda_{qq'}(\mu,\nu)$ is given by

$$\Lambda_{qq'}(\mu,\nu)=-g^2\beta^2(3q_{\mu\nu}q_{\mu\nu}'-\delta_{qq'}r_{\mu\nu}^2)r_{\mu\nu}^{-5}. \tag{8}$$

The q component of the spin operator for the μth electron is $S_{\mu q}$. We note that $\Sigma\,\Lambda_{qq}=0$ and the matrix of $\mathcal{H}_D$ has zero trace. Writing the matrix elements $\langle\Psi_j(\Gamma)\mid\mathcal{H}_D\mid\Psi_j(\Gamma)\rangle$ as D_{jj} it follows that:

$$D_{00}=-2D_{11}. \tag{9}$$

Thus the zero-field splitting parameter D [Eq. (5)] is identified as

$$D=3D_{11}. \tag{10}$$

This is a useful form because D_{11} can be simplified readily to integrals over molecular orbitals, yielding for $\Gamma=A_1''$,

$$\begin{aligned}-D/3&=\langle n_{+2}(1)\pi_{+2}(2)-n_{+2}(2)\pi_{+2}(1)\mid\Lambda_{zz}\mid n_{-2}(1)\pi_{-2}(2)\rangle\\&\quad-\langle n_{+2}(1)\pi_{-2}(2)-n_{+2}(2)\pi_{-2}(1)\mid\Lambda_{zz}\mid n_{+2}(1)\pi_{-2}(2)\rangle.\end{aligned} \tag{11}$$

The D values for the states A_2'' and E'' are obtained in a similar manner. These quantities can now be simplified into integrals over atomic orbitals, and in the one-center approximation we obtain (again for $\Gamma=A_1''$)

$$D^{(1)}=\tfrac{1}{2}\langle\sigma(1)p_z(2)-\sigma(2)p_z(1)\mid\Lambda_{zz}\mid\sigma(1)p_z(2)\rangle, \tag{12}$$

where σ is a nonbonding orbital and p_z is a $2p$ orbital

of nitrogen. For our previous estimates of spin–spin interactions[5,9,10] we have used a frozen-core approximation. For triazine we had used Brinen and Goodman[4] wavefunctions for A_1''. In the present study we have calculated both the Coulomb and exchange-type integrals by the Fourier convolution method and also used the values of some published integrals.[9,11] Slater-type atomic orbitals, conventional exponents, and the choice of sp^2 hybrid atomic orbitals for σ, yields

$$D^{(1)} = -0.032 \text{ cm}^{-1}, \qquad (13)$$

when the σ orbitals are chosen as, $\alpha\phi(2s)+\beta\phi(2p)$, we obtain $D^{(1)}=-0.048\beta^2$ cm^{-1} which gives the above result for $\beta^2=\frac{2}{3}$. We expect the two-center terms to be small because they will be concerned with σ (on-one-atom)$-p_z$ (on-the-other-atom) overlap.

DISCUSSION

The sign of D for *s*-triazine is different from that of benzene and this could be caused by the importance of one-center spin–spin interactions in the case of *s*-triazine. For benzene in a $\pi\pi^*$ state the x and y spin substates are at higher energy than z because the interaction is repulsive for two parallel dipoles at different atoms. In *s*-triazine the two parallel dipoles are at the same center in a σp_z configuration, the interaction is therefore attractive and the z spin subtrate is caused to be at highest energy. The value of D for triazine is considerably smaller than that for pyrazine[10] which derives from the same interactions. The difference may be that the effective electron density at a nitrogen in triazine is less than for the appropriate configurations of pyrazine: Simple MO considerations indicate a fourfold increase of σp_z density for pyrazine over *s*-triazine. There are expected to be nearby $^3E''$ states but these will not influence D since the $^3A_1''$–$^3E''$ spin–orbit interaction vanishes by symmetry.

Since there are no strong singlet–triplet transitions (heavy atoms) seen or expected in *s*-triazine, the crystal-field effects on the triplet-state intensity are expected to be dominated by the interactions among singlet states. Thus the Zeeman effect selection rules are not altered,[12] and the only differences expected between neat crystal and isolated molecule studies is the apportionment of electric dipole strength amongst the spin sublevels. Therefore the $^3A_1''$ assignment seems fairly certain. This is confirmed by the fact that this transition does not split in an electric field.

We note again[5,13] that the occurrence of an $n\rightarrow\pi^*$ transition exhibiting out-of-plane polarization, is an event that is hardly encompassed by the usual generalizations regarding azine singlet–triplet transitions. This is a case where the sources of in-plane intensity are energetically less accessible than is normally the case for *N*-heterocyclics, whereas the $^1A_2''$ state is probably quite nearby.

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